

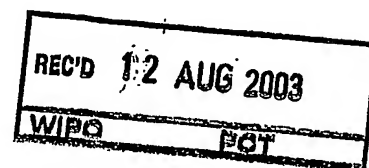
10/522597

PCT/DK 03/00499

10 Rec'd PCT/PTO

DK 03/0499

25 JAN 2005



Kongeriget Danmark

Patent application No.: PA 2003 00654

Date of filing: 01 May 2003

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Title: Method of treating af surface, coating compositions and use thereof and coated surfaces obtainable by the use (2)

IPC: -

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05. August 2003

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PATENT- OG VAREMÆRKESTYRELSEN

METHOD OF TREATING A SURFACE, COATING COMPOSITIONS AND USE
THEREOF AND COATED SURFACES OBTAINABLE BY THE USE (2)

DESCRIPTION

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1. BACKGROUND OF THE INVENTION

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The present invention relates to a method of treating exposed surfaces, e.g. for use in protection treatment of e.g. monuments, buildings and constructions having surface structures made of i.a. steel, aluminium, sandstone, marble, granite, slate, cement, fibre-reinforced cement, bricks, tiles, fibre glass-reinforced materials, and wood, as well as public and private transportation vehicles like busses, trains, trolleys, etc., and road and traffic signs, turbine blades, e.g. wind mill turbine blades, against graffiti and/or pollution, but also for use in anti-fouling treatment of underwater structures, e.g. ship hulls, and exposed surfaces obtainable by the method, and use thereof.

20

As used in the specification and claims, the term "graffiti" means any unwanted painting, drawing, lettering or other marking formed on a surface.

25

Although many countries have adopted strict environmental regulations which are intended to protect the environment against pollution from i.a. waste and combustion products, formation of deposits on and corrosion of surfaces of buildings, construction materials, public and private transportation vehicles, etc., caused by pollution still continue to cause problems.

30

Thus, it is desired to prevent formation of and/or remove such deposits of waste and combustion products, in particular smog; to prevent formation of reaction products formed by i.a. acid rains, sulphur oxides, and nitrogen oxides; and to provide easy removal of graffiti paintings on such surfaces.

Cleaning of such surfaces to remove pollution deposits, including graffiti, often requires application of high-pressure sand blasting treatments or treatment with hot steam or aggressive and hazardous chemical cleaning agents. Also, following such cleaning treatment the surfaces often have to be further renovated, and application of new surface treatments or paintings may be required.

Similarly anti-fouling treatment of ship hulls requires frequent cleaning and surface treatment, including high-pressure sand blasting treatments or treatment with aggressive and hazardous chemical cleaning agents, often followed by application of new paintings and/or fouling agents.

In particular for anti-fouling products, new very strict legislation is coming into force in several countries in order to prevent use of biocides, TBT, and heavy metals, which are presently polluting the water environment. Therefore, heavy efforts have been done to provide non-poisonous anti-fouling coatings.

Consequently, there is a need for an improved method and means for treating surfaces of buildings, construction materials, public and private transportation vehicles, ship hulls, etc., whereby less complicated cleaning methods are required to remove pollution or fouling deposits; and whereby application of environmentally hazardous agents, renovation and repainting can be avoided or reduced.

2. DISCLOSURE OF THE INVENTION

Object of the Invention

It is an object of the present invention to provide an improved method of treating a surface, in particular to provide an improved method of providing a surface with a protecting coating.

In particular, it is an object of the present invention to provide improved methods of

1. providing a surface with an essentially permanent anti-graffiti coating;
2. providing a surface with an essentially permanent coating protecting against pollution and corrosion; and
3. providing an under water structure, e.g. a ship hull, with an essentially permanent anti-fouling coating.

Another object of the present invention is to provide a coating composition, in particular an anti-graffiti coating composition, which is inexpensive to manufacture, easy to apply, and environmentally safe in use.

Further objects appear from the description elsewhere.

Statement of Invention

According to an aspect of the present invention, there is provided a method of treating a surface comprising the steps of

- providing a coating composition comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase;
- applying said coating composition to the surface;
- evaporating said liquid phase from the applied coating composition; and
- subjecting said dried, applied coating composition to a heating treatment to coalesce said wax particles.

In this text the term "polyolefin" is intended to designate: "A polymer prepared by the polymerization of olefins as the sole monomers, copolymers thereof as well as oxidized and or halogenated, in particular fluorinated derivatives thereof".

5 The term "a mixture of polyolefin waxes" is intended to designate: "A macroscopically homogeneous mixture of two or more different species of polymer, including cases, where the blends are homogeneous on scales smaller than several times visual optical wavelengths".

10 A polyolefin wax is characterized by an intermediate number of carbon atoms in the polyolefin backbone as explained in the following. The number of carbon atoms in a carbon hydride, n , in the carbon backbone, C_n , determines the physical state of the substance at room temperature and atmospheric pressure: C_1 to C_4 corresponds to a gaseous state, C_5 to C_8 corresponds to a liquid state,
15 C_9 to C_{500} corresponds to a waxy solid state, and well above 500 carbon atoms corresponds to a macromolecule, a resinous polymer. The above values for n are meant for illustrating purposes only for illustrating the transition from a gaseous state to a solid state upon increasing n . The actual value of n for a given real material depends on the type of the monomer used in manufacturing
20 the carbon hydride molecules.

One advantage of using a polyolefin wax is believed to be the ability of the polyolefin wax to flow in a heating treatment at elevated temperatures, thus being a liquid with a low viscosity, and subsequently during and after the heating treatment, consolidating to a thin coating of a solid state polymer with chemical inertness and mechanical resistance.
25

In one embodiment the polyolefin wax is selected from the group consisting of a homopolymer, a co-polymer, a block-copolymer and a random copolymer and mixtures thereof.
30

One advantage of using a polyolefin wax, as a coating material is the low surface energy exhibited by polyolefins.

5 Other advantages of using particles of a polyolefin wax material are stated below with reference to i.a. the material parameters of chemical composition, molecular structure, melt index, viscosity, melt flow ratio, particle size.

10 A polyolefin wax may also be defined as a polymer of an olefin, which polymer has a low polymerization degree.

In one embodiment the polyolefin wax is essentially a polyethylene wax.

15 In one embodiment the polyolefin wax or at least one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polyethylene wax.

20 In one embodiment the polyethylene wax is having a degree of polymerisation between 10 and 500, in particular between 20 and 300, in particular between 30 and 200, in particular between 30 and 150, in particular between 30 and 100.

The degree of polymerisation is defined as the number of monomers polymerized to form the polymer.

25 In one embodiment the particle size of the polyethylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm . According to an aspect of the invention the particle size is relatively small such that substantially the entire particle is softening upon the heating treatment, thus leaving substantially none of the inner volume of the particle unaffected by the heating treatment, such that the particle is capable of coalescing with the other
30 particles.

In one embodiment the peak melting point of the polyethylene wax is between 70 and 145°C, preferably between 80 and 140°C, in particular between 90 and 135°C, in particular between 95 and 120°C. The peak melting point may be determined by a differential scanning calorimetry (DSC) method that provides a thermogram, a plot of the instantaneous heat capacity as a function of temperature. The peak melting point is taken as the peak of the thermogram-plot.

In one embodiment the polyethylene wax is consisting of linear polyethylene molecules.

In one embodiment the polyethylene wax is characterised as high-density polyethylene, HDPE. HDPE have densities falling in the range of 0.94-0.99 g/cm³ and it consists of primarily unbranched polyethylene.

In one embodiment the polyethylene wax has a viscosity at 149 °C of 300 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less, preferably 20 mPa s or less, preferably 10 mPa s or less, preferably 5 mPa s or less. The values are taken as zero shear viscosity values. The zero shear viscosity is the apparent viscosity at zero shear rate and is not a directly measurable value, but can be obtained by extrapolation from observed viscosities over a range of finite shear rates. In one embodiment of the invention the viscosity of the polyolefin wax undergoes a transition to a lower value quickly, relative to the time the polyolefin wax particles are subjected to non-excessive heating. By "non-excessive heating" is meant a heating condition where the chemical structure of the particle material is not compromised, and/or the substrate material subjected to the heating treatment is not compromised.

In one embodiment the polyethylene wax has a molecular weight distribution, M_w/M_n , of 1 to 25, preferably of 1 to 10, preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2. In the traditional

way of determining the parameters of M_W and M_n the M_W -value is always lower or equal to the value of M_n , see "Handbook of polyethylene", A.J. Peacock, Marcel Dekker Inc., 2000, pp. 7-10 for a definition of M_W and M_n and their relationship. The parameter of melt flow ratio is an approximate measure for the parameter of molecular weight distribution as a general trend. A low melt flow ratio is preferred in order to let all the polyolefin wax molecules respond uniformly to the heating treatment.

In one embodiment the polyethylene wax has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_W/M_n , of 6,0 or less, preferably has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_W/M_n , of 4,0 or less, more preferably a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_W/M_n , of 2,0 or less.

The polyolefin wax particles preserve their shapes during the evaporation of the liquid phase from the applied coating composition and the particles are essentially left in a dried state when substantially all the liquid phase has evaporated.

"Coalesce"/"coalescence" is intended to designate: "to form/ the formation of a coherent phase from an incoherent phase of separate particles by fusion or growing together of the particles".

In one embodiment of the invention the particle material is a polyolefin wax, which has an advantageous value of all or nearly all of the following physical parameters and characteristics: chemical inertness, mechanical resistance, melt index, viscosity, melt flow ratio and particle size.

In one embodiment the polyethylene wax has a degree of polymerisation between 10 and 500, in particular between 20 and 300, in particular between 30

and 200, in particular between 30 and 150, in particular between 30 and 100 and a particle size between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm , and a peak melting point between 70 and 145°C, preferably between 80 and 140°C, in particular between 90 and 135°C, in particular between 95 and 120°C, and a viscosity at 149 °C of 300 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less, preferably 20 mPa s or less, preferably 10 mPa s or less, preferably 5 mPa s or less, and a molecular weight distribution, M_w/M_n , of 1 to 10, preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2.

In one embodiment the polyolefin wax is essentially a polypropylene wax.

In one embodiment the polyolefin wax or at least one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polypropylene wax.

in one embodiment the polyolefin wax or at least one of the components in the mixture of polyolefin waxes suspended in the coating composition is a co-polymer of propylene and one or more other olefins not including propylene.

In one embodiment the particle size of the polypropylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

In one embodiment the peak melting point of the polypropylene wax is between 70 and 200°C, preferably between 100 and 170°C, in particular between 110 and 160°C, in particular between 120 and 150°C.

In one embodiment the polypropylene wax is consisting of essentially unbranched polypropylene molecules. A decrease in branching of the polypropylene molecules results in a narrower melting distribution.

- 5 In one embodiment the polypropylene wax is characterised as consisting of essentially isotactic polypropylene molecules. Isotactic polypropylene consists of molecules in which all methyl groups have the same stereochemistry as a result of all insertions of propylene monomer being identical.
- 10 In one embodiment the polypropylene wax is characterised as consisting of essentially syndiotactic polypropylene molecules. Regular alternating stereochemistry of monomer insertion, resulting in alternating locations of the pendent methyl groups, produces syndiotactic polypropylene.
- 15 In one embodiment the polypropylene wax is characterised as consisting of essentially stereo block polymer structures, i.e. molecules having segments being syndiotactic or isotactic. In one embodiment the polypropylene comprises atactic polypropylene exhibiting random location of the pendent methyl groups.
- 20 In one embodiment the polypropylene wax has a viscosity at 190 °C of 400 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less.
- 25 In one embodiment the polypropylene wax has a melt flow at 230 °C/2.16 kg of 40 g/min or more, preferably 100 g/min or more, preferably 500 g/min or more, preferably 1000 g/min or more, preferably 4000 g/min or more, preferably 8000 g/min or more.

The melt flow is measured as the weight of molten polymer flowing at 230 °C for 10 min. through a 2.095-mm diameter die at a 2.16 kg load according to ASTM test D1238L.

5 In one embodiment the polypropylene wax has a molecular weight distribution, M_w/M_n , of 1 to 25, preferably of 1 to 10, preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2.

10 The alkanes of the polyolefin wax may have a molecular weight distribution that is essentially symmetric when plotted on a semi-logarithmic scale. The peak molecular weight M_p , defined as the molecular weight at the maximum of the molecular weight distribution, may fall between the number- M_n , and weight-average M_w molecular weight values for a normal distribution curve. In one embodiment the molecular weight distribution is homogenous and unimodal.

15 In one embodiment the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition consists essentially of one or more of the alkanes selected from the group of alkanes determined by the generic formula $\text{CH}_3\text{CHR}_1-(\text{CH}_2\text{CHR}_1)_n-\text{CHR}_1-\text{CH}_3$ for n equal to:
 20 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, where $R_1 = \text{H}$ or CH_3 .

25 In one embodiment the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition consists essentially of one or more of the alkanes selected from the group of alkanes determined by the generic formula $\text{CH}_3\text{CHR}_1-(\text{CH}_2\text{CHR}_1)_n-\text{CHR}_1-\text{CH}_3$ for n equal to:
 30 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140,

141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, where $R_1 = H$ or CH_3 .

10 The synthetic wax may be synthesized by a high-pressure polymerization or a low-pressure (Zeigler-type catalysts) polymerization. It may be a by-product produced in making polyethylene plastic resin. Further, it may be distilled under vacuum to obtain a narrower molecular weight distribution.

15 In one embodiment the process of manufacturing the polyolefin wax is based on the Fischer-Tropsch synthesis.

In one embodiment a metallocene catalyst is used in the process of manufacturing the polyolefin wax.

20 In one embodiment the alkanes has a number of alkyl groups situated on the carbon backbone of the alkanes as branches, which number is 30 or less, preferably 20 or less, more preferably 10 or less, even more preferably 5 or less.

25 In one embodiment the alkyl groups situated on the carbon backbone of the alkane are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, preferably from the group consisting of ethyl, butyl, hexyl, octyl, more preferably from the group consisting of ethyl and butyl, yet more preferably is ethyl.

30

In one embodiment $R_1 = \text{CH}_3$ and all the methyl groups have the same stereochemistry.

5 In one embodiment $R_1 = \text{CH}_3$ and the stereochemistry changes from one methyl group to a neighbouring other methyl group.

In one embodiment $R_1 = \text{CH}_3$ and the molecular structure is a stereo block.

10 In one embodiment the polyolefin wax re-crystallizes to form another crystal structure than the crystal structure of the polyolefin wax particles of the coating composition upon allowing said heat treated coating composition to consolidate to a protective coating. In one embodiment the process associated with the consolidation of a protective coating results in amorphous regions of polyolefin wax and/or interfacial regions between crystalline and amorphous regions. The definition of "crystalline region", "amorphous region", and "interfacial region" can be
15 found in "Handbook of polyethylene", A.J. Peacock, Marcel Dekker Inc., 2000, p. 68 and the accompanying figure 1, which is hereby incorporated by reference.

20 In one embodiment the polyolefin wax is an oxidized polyethylene wax, with an acid number in the interval of 1 to 100 mg KOH/g, preferably in the interval of 1 to 40 mg KOH/g, more preferably in the interval of 1 to 30 mg KOH/g, even more preferably in the interval of 2 to 20 mg KOH/g, yet more preferably in the interval of 2 to 10 mg KOH/g.

25 In one embodiment the polyolefin wax is the polyethylene wax, Shamrock S-394, SP 5, average particle size: 18 μm , from Shamrock Technologies, specific gravity: 0.95 g/cm³, DSC melt point: 113°C, Softening point: 99°C.

30 In one embodiment the polyolefin wax is the polyethylene wax, Shamrock S-394, N 5, average particle size: 12.5 μm , from Shamrock Technologies, specific gravity: 0.95 g/cm³, DSC melt point: 113°C, Softening point: 99°C.

In one embodiment the polyolefin wax is the polyethylene wax, Shamrock S-394, N 1, average particle size: 5 μm , from Shamrock Technologies, specific gravity: 0.95 g/cm^3 , DSC melt point: 113°C, Softening point: 99°C.

5 In one embodiment the polyolefin wax is the polyethylene wax, DAVOSI, supplied by Dansk Voksfabrik A/S, Copenhagen, specific gravity: 0.96-0.98 g/cm^3 , drop forming point (DGF-M-III 3): 125°C.

10 In one embodiment the polyolefin wax is the POLYWAX 500 from Baker Petrolite, melt point approx. 71 °C. In one embodiment the polyolefin wax is the POLYWAX 655 from Baker Petrolite, melt point approx. 87 °C. In one embodiment the polyolefin wax is the POLYWAX 850 from Baker Petrolite. In one embodiment the polyolefin wax is the POLYWAX 1000 from Baker Petrolite, melt point approx. 103 °C. In one embodiment the polyolefin wax is the POLYWAX 2000 from Baker Petrolite, melt point approx. 112 °C. In one embodiment the polyolefin wax is the POLYWAX 3000 from Baker Petrolite, melt point approx. 115 °C. All the above-mentioned POLYWAX products are ethylene homopolymers, which are linear and characterised by a molecular weight distribution, M_w/M_n of approximately 1.1 and are highly crystalline.

20 In one embodiment the polyolefin wax is the Polypropylene copolymer wax powder, Shamrock S 363, Average particle size: 5 μm , Specific gravity: 0.94 g/cm^3 , DSC melt point: 140°C, Softening point: 68°C.

25 In one embodiment the coating composition is the PTFE: 60 % aqueous dispersion of polytetrafluorethylene, Shamrock FLUORO AQ 60, Average particle size: 2-3 μm , pH: 7-8, Apparent density: 1.47

30 According to another aspect of the present invention, there is provided a method of providing a surface with a protecting coating by

- applying a coating composition in the form of a suspension comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase to the surface;

5 - evaporating said liquid phase from the applied coating composition;

10 - subjecting said dried, applied coating composition to a heating treatment to raise the temperature of the dried coating composition to bring said particles of a polyolefin wax or of a mixture of polyolefin waxes into a coalescing state allowing said wax particles to provide a continuous coating of the surface; and

15 - allowing said heat treated coating composition to consolidate to a protective coating.

20 The liquid phase should be based on a liquid or a mixture of liquids which are readily vaporizable at a relatively low temperature, i.e. about 50 to 110°C; environmentally acceptable; and suitable for carrying a suspension of particles of polyolefin wax.

25 The evaporation step can be carried out by allowing the applied coating composition to evaporate at room/ambient temperature, but heat may also be applied using well-known heating apparatus.

30 The heating treatment by which the wax particles are brought into a coalescing state can be carried out using well-known heating apparatus, e.g. using IR radiation or hot air or hot gas.

 According to preferred embodiments of these methods the liquid phase of the coating composition has a boiling point or a boiling point range lower than the

melting point or melting point range of the particles of the polyolefin wax or of the mixture of polyolefin waxes.

5 Hereby it may be obtained that liquid phase is essentially evaporated before the temperature of the wax particles becomes so high that they enter into the coalescing state, i.e. before the continuous coating of the surface is formed.

10 The melting point or melting point range of the particles of the polyolefin wax or of the mixture of polyolefin waxes may preferably be between 60 and 250 °C, in particular between 90 and 140 °C.

According to preferred embodiments the liquid phase of the coating composition is organic.

15 The liquid phase of the coating composition may consist essentially of a member of the group consisting of ethers, esters, ketones, alcohols and mixtures thereof.

20 It may comprise an alcohol, preferably ethyl alcohol, and optionally water, whereby the concentration of water, calculated on weight basis, in the liquid phase may be up to 50 %.

In one embodiment the liquid phase of the coating composition comprises an alcohol, preferably ethyl alcohol.

25 According to other preferred embodiment the liquid phase of the coating composition may be essentially aqueous.

30 In one embodiment the liquid phase of the coating composition consists essentially of ethyl alcohol, 96% ethanol.

In one embodiment the liquid phase of the coating composition comprises an alcohol, preferably ethyl alcohol, and water.

In one embodiment the coating composition contains, calculated on weight basis:

- 5 - polyolefin wax/mixture of polyolefin waxes 1 - 25 %, preferably 9 - 13
 %, - liquid phase 99 - 75 %, preferably 91 - 87 %.

10 Further, the coating composition may comprise one or more auxiliary agents selected from the group consisting of diluting agents, dispersing agents, conservation agents, emulsifying agents, and colouring agents, whereby the coating composition, calculated on weight basis, may contain up to 10% auxiliary agents.

15 The colouring agents may be selected from colouring agents based on dyes or pigments.

20 According to other preferred embodiments the coating composition is consisting essentially of particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid organic or aqueous phase and one or more auxiliary agents selected from the group consisting of diluting agents, dispersing agents, conservation agents, emulsifying agents, and colouring agents.

25 A preferred polyolefin wax has the characteristics of being easily dispersed in a liquid phase. In one embodiment the polyolefin wax disperses with substantially no additives to improve the dispersion process.

 In one embodiment the coating composition is consisting essentially of particles of a polyolefin wax suspended in a liquid phase.

30 In one embodiment the coating composition is consisting essentially of particles of a mixture of polyolefin waxes suspended in a liquid phase.

In one embodiment the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition are selected from the group consisting of polyethylene waxes, polypropylene waxes and oxidized and/or halogenated, in particular fluorinated polyethylene and polypropylene waxes.

5

According to another preferred embodiment the polyolefin wax or one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polytetrafluorethylene wax.

10 However, polytetrafluorethylene wax is preferably used in mixtures or alloys with other polyolefin waxes.

The particle size of the polytetrafluorethylene wax may be between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm , and the
15 melting point of the polytetrafluorethylene wax may be between 250 and 360°C, preferably between 260 and 330°C, in particular between 280 and 320°C.

The application of the coating composition can be carried out using any suitable application technique including brushing, wiping, or rolling according to a preferred embodiment the coating composition is applied to the surface by spraying.
20 In one embodiment the coating composition resulting from dispersing the polyolefin wax in the liquid phase, is capable of being applied to the surface to be coated, preferably without using high-pressure applications. The coating composition is preferably capable of being applied with a spray bottle worked by hand.

25 When the method is used as protection treatment against graffiti the coating composition is applied in an amount effective to prevent graffiti markings applied to the coated surface from penetrating through the protective coating to the underlying surface.

30

When the method is used as protection treatment against attack by aggressive gases or liquids the coating composition is applied in an amount effective to prevent the aggressive gases or liquids contacting the coated surface from penetrating through the protective coating to the underlying surface.

5

According to a preferred embodiment the coating composition is applied to the surface in an amount of 50 to 350 ml per m².

10

The amount of the applied coating composition is determined by the porosity and nature of the surface to be treated or protected. Further, the weight percentage of the polyolefin wax/mixture of polyolefin waxes in the coating composition is also determined by the porosity and nature of the surface to be treated or protected.

15

Typical concentrations and amounts of the applied coating composition appears from the following table 1:

Table 1

	Composition (g wax powder/litre liquid)	Coverage (ml coating composition/m ²)
Porous substrates	140 - 150	125 - 350
Steel/painted surface	10 - 15	50 - 85
Stone, marble, slate etc.	65 - 75	60 - 170

20

According to another aspect of the present invention, there is provided a coating composition comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase.

5 The coating compositions are prepared by suspending a selected amount of polyolefin wax or the mixture of polyolefin waxes in a selected amount of a selected liquid, e.g. water or ethyl alcohol, if desired in the presence of dispersion agents, in a manner known per se, e.g. as further disclosed in the examples.

Preferred embodiments are disclosed in claims 50 to 95.

10 According to other aspects of the present invention, there is provided a

- use of the coating composition according to any of claims 50 to 95 for treating a surface;

15 - use of the coating composition according to any of claims 50 to 95 for providing a surface with an essentially permanent anti-graffiti coating;

20 - use of the coating composition according to any of claims 50 to 95 for providing a surface with an essentially permanent coating protecting against pollution and corrosion; and

- use of the coating composition according to any of claims 50 to 95 for providing an under water structure, e.g. a ship hull, with an essentially permanent anti-fouling coating.

25 According to other aspects of the present invention, there is provided an

- article of manufacture comprising a structure with a surface coated by the method according to any of claims 1 to 49; and

30 - article of manufacture comprising a structure with a surface coated by use of the coating composition according to any of claims 50 to 95.

In one embodiment the article is the set of blades of a turbine, such as a windmill turbine. One advantage of using the method according to any of claims 1 to 49 and/or the coating composition according to any of claims 50 to 95 is to provide the blades with a durable and protective surface coating.

In one embodiment the article is a tank for fluids or solid substances, e.g. a metal tank or a glasfibre tank. One advantage of using the method according to any of claims 1 to 49 and/or the coating composition according to any of claims 50 to 95 is to provide the metal tank with a durable and protective surface coating.

In one embodiment the article is a plate made of eternit (fibre cement), particular for the roofing and facing purposes for buildings. One advantage of using the method according to any of claims 1 to 49 and/or the coating composition according to any of claims 50 to 95 is to provide plates made of eternit (fibre cement) with a durable and protective surface coating.

The invention will now be illustrated by way of the following examples which are for the purpose of illustration only and are in no way as to be considered limiting. In the following examples all parts and percentages are by weight and all temperatures and degrees are Celsius unless otherwise indicated.

3. EXAMPLES

Preferred embodiments of the invention are further illustrated by examples which are for the purpose of illustration only and are in no way as to be considered limiting.

The materials used in the examples were as follows:

Waxes:

Carnauba Wax: Carnauba Wax, Type CARNAUBA CARE 100, from Brenntag Nordic, Melting point: 80 – 86 °C, Acid value (ASTM D 1386): 2-7.

5 Ceresin wax: Ceresin wax powder, Specific gravity: 0.8 g/cm³, Boiling point approx. 300°C, Melting point 57 – 59 °C.

PE (1): Polyethylene wax powder, DAVOSI, Specific gravity: 0.96-0.98 g/cm³, Drop forming point (DGF-M-III 3): 125°C

10 PE (2): Polyethylene wax powder, Shamrock S 394, N1, Average particle size: 5 µm,
Specific gravity: 0.95 g/cm³, DSC melt point: 113°C, Softening point: 99°C

15 PE (3): Polyethylene wax powder, Shamrock S 394, SP 5, Average particle size: 18 µm,
Specific gravity: 0.95 g/cm³, DSC melt point: 113°C, Softening point: 99°C

20 PP (1): Polypropylene copolymer wax powder, Shamrock S 363, Average particle size: 5 µm, Specific gravity: 0.94 g/cm³, DSC melt point: 140°C, Softening point: 68°C

PTFE (1): 60 % aqueous dispersion of polytetrafluorethylene, Shamrock FLUORO AQ 60, Average particle size: 2-3 µm, pH: 7-8, Apparent density: 1.47

25 Solvents/Acids:

Oil: Paraffin oil pharmaceutical grade, Parafluid type PL501A from Parafluid Mineralölgesellschaft GmbH, Hamburg, Germany

30 Acetone: Commercial grade, Borup Kemi AS, Denmark

Xylene: Commercial grade, Borup Kemi AS, Denmark

White Spirit: Commercial grade, Borup Kemi AS, Denmark

5

Alcohol: Denaturated Ethyl alcohol, Commercial grade, Borup Kemi AS, Denmark

Concentrated Sulphuric Acid: 96% Commercial grade, Borup Kemi AS, Denmark

10

Water: Tap water

Auxiliary agents:

15

Coloring Agent: Aquatop Teknomix 2990 from Teknos Denmark AS

Comparison tests:

Comparison example A (carnauba wax)

20

Surface: Concrete plate 90 x 160 mm.

A mix of oil and Carnauba wax (90:10) was heated in small container until melting of the wax. Immediately after the mix was applied by brush on to the concrete plate.

25

Dried for 24 hours at 20 degrees C, 65% rel. humidity.

Then a solvent based graffiti paint was spayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% rel. humidity.

30

Then the graffiti was subjected to high pressure (water, 90 -100 bar) cleaning

Result: The graffiti could not be removed by high pressure (water 90 -100 bar) cleaning.

5

Comparison example B (ceresin wax)

Surface: Concrete plate 90 x 160 mm.

10

A mix of oil and Ceresin wax (90:10) was heated in a small container until melting of the wax. Immediately after the mix was applied by brush on to the concrete plate in a thin layer.

Dried for 24 hours at 20 degrees C, 65% rel. humidity.

15

Then a solvent based graffiti paint was sprayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% rel. humidity.

Then the graffiti was subjected to high pressure (water, 90 -100 bar) cleaning

20

Result: The graffiti could not be removed by high pressure (water 90 -100 bar) cleaning.

Examples according to the present invention

25

The following coating compositions were prepared and used in the following examples:

30

Coating composition	PE(1) (PPW)	PE(2) (PPW)	PE(3) (PPW)	PP(1) (PPW)	PTFE(1) (PPW)	Alcohol (PPW)
1	10					1000
2		10				1000
3			10			1000
4				10		1000
5					10	1000

Example 1 (PE (1) Davosi – Polyethylene wax powder)

5 Surface: Glass plates 70x150 mm; Steel plates 150x150 mm Quantity
applied: $6.7 \cdot 10^{-5}$ ml/cm²

10 The wax mix was applied by airless spray gun on to the steel plates and dried for
3 hours. It was observed that the surface of the test specimen was covered by a
white wax powder. Then the surface of the test specimen were heated by a
Ripack 2000 gas heated gun until the white wax powder was melting and be-
come transparent.

15 Cured for 12 hours at 20 degrees C, 65% relative humidity

Then solvent based graffiti paint was spayed on to the coated surface and cured
for 24 hours at 20 degrees C, 65% relative humidity.

Observations:

20 The graffiti was easily removed by a brush and lukewarm water as well as by
high pressure cleaning (water, 90-100 bar).

Similar tests were carried out on the following test specimen substrates:

1. Steel plates with car lacquer 100 x 100 mm
2. Concrete plates 100 x 100 mm
3. Slate plates, smooth, 100 x 100 mm
4. Slate plates, rough, 100 x 100 mm
5. Granite plates, smooth 100 x 100 mm
6. Granite plates, rough 100 x 100 mm
7. Marble plates, smooth 100 x 100 mm
8. Sand stone plates, 100 x 100 mm

10 Observations for all layers:

The graffiti was easily removed by a brush and lukewarm water as well as by high pressure cleaning (90-100 bar).

15 On one of the test steel specimen up to 50 repetitive layers of graffiti paint was applied and removed on the same wax coating.

20 To test the wear resistance on another of the test specimen steel plates 1000 repetitive grindings (of 30 seconds each) made with a 3M hard, green kitchen sponge. Then solvent based graffiti paint was sprayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% relative humidity.

Further observation:

25 On non heated surfaces the wax coating was easily removed by a cloth or a soft sponge.

30 On one of the sandstone specimens, coated on one side only, a solvent based graffiti paint was sprayed on as described in the above on both the coated side as well as on the non coated side.

Observations:

On the coated side the graffiti was easily removed by a brush and lukewarm water as well as by high pressure cleaning (water, 90-100 bar). On the non
5 coated side the graffiti could not be removed.

Then concentrated sulphuric acid was applied in a thin layer on approx. 50% of the coated side.

10 90 minutes later the acid was removed by clean water and the surface was dried.

Observations:

No visible attack from the sulphuric acid was detected.

15 1 hour later a new layer of graffiti paint was applied and cured as previously described.

Observations:

20 The graffiti was easily removed by a brush and lukewarm water as well as by high pressure cleaning (90-100 bar).

On the non coated side a similar test with sulphur acid was made.

Observations:

The graffiti paint was diluted/destroyed by the acid, which has also started to deteriorate the surface of the sandstone.

To investigate the effect of the heating treatment of the wax composition a number of specimens with a diameter of approx. 60mm and a thickness of up to 15 mm were molded by heating up approx. 15 g of wax powder in a metal cup.

5 4 specimens were dyed into brown respectively blue, green and black colors.

The molded specimens were submerged into various liquids such as:

- 10
1. Concentrated Sulphuric Acid
 2. Alcohol
 3. White Spirit
 4. Xylene
 5. Acetone
 6. Tap water

15

Observations after 21 days:

No damages or any kind of visible deterioration of the specimens were detected.
No coloring of the liquids was observed.

20

1 colored specimen was submerged into sea water for 18 months.

Observation:

No damages or any kind of visible deterioration were detected.

25

Test for diffusion openness

30

To evaluate the diffusion openness a test was carried out on a plate of concrete (100 x 150 x 12mm) treated as previously described on all sides with the exception of a circle with a diameter of 40mm on one of the sides.

Exactly on the said circle a glass tube with a diameter of 40mm and a height of 600 mm was glued on to the steel plate with silicone.

5 The tube was filled with 500 mm clean water and the plate was placed on 4 pieces of wood in each corner to raise it from the table plate.

Observation:

10 After 5-10 seconds the water began to drip very fast through the coated concrete plate.

Test on traffic sign:

15 On a special light reflection treated traffic sign a test was carried out to verify whether the degree of light reflection was reduced by our coating.

20 The wax mix was applied by airless spray gun on to the steel plates and dried for 3 hours. Then the surface of the test specimen were heated by a Ripack 2000 gas heated gun until the white wax powder was melting and become transparent.

Cured for 12 hours at 20 degrees C, 65% relative humidity

25 Light test carried out during the night time proved that the coating do not have any adverse effect of the light reflection.

Test of discoloration on coated surfaces:

30 Observations from a wide range of various test of numerous substrates has showed that change in colors and/or gloss is extremely small. Even on non painted steel only an extremely limited darkening and increase of gloss can be observed.

Test of protection against moss and algae:

Observations from a range of tests on concrete and steel have showed that the coating has a pronounced effect to avoid or strongly reduce growth of moss and algae in moist and wet environments.

Example 2 (PE (2) Shamrock S 394, N1 – Polyethylene wax powder)

Surface: Glass plates 70x150 mm; Steel plates 150x150 mm Quantity
applied: $6.7 \cdot 10^{-5} \text{ ml/cm}^2$

The wax mix was applied by airless spray gun on to the steel plates and dried for 3 hours. Then the surface of the test specimen were heated by a Ripack 2000 gas heated gun until the white wax powder was melting and become transparent.

Cured for 12 hours at 20 degrees C, 65% relative humidity

Then solvent based graffiti paint was sprayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% relative humidity.

Observations:

The graffiti was easily removed by a brush and lukewarm water as well as by high pressure cleaning (water, 90-100 bar).

Example 3 (PE (3) Shamrock S 394, SP5 – Polyethylene wax powder)

Surface: Glass plates 70x150 mm; Steel plates 150x150 mm. Quantity applied:
 $6.7 \cdot 10^{-5} \text{ ml/cm}^2$

The wax mix was applied by airless spray gun on to the steel plates and dried for 3 hours. Then the surface of the test specimen were heated by a Ripack 2000 gas heated gun until the white wax powder was melting and become transparent.

5 Cured for 12 hours at 20 degrees C, 65% relative humidity

Then solvent based graffiti paint was sprayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% relative humidity.

10 Observations:

The graffiti was easily removed by a brush and lukewarm water as well as by high pressure cleaning (water, 90-100 bar).

15 Example 4 (PP (1)) Shamrock S 363, – Polypropylene wax powder)

Surface: Glass plates 70x150 mm; Steel plates 150x150 mm. Quantity applied: $6.7 \cdot 10^{-5} \text{ ml/cm}^2$

20 The wax mix was applied by airless spray gun on to the steel plates and dried for 3 hours. Then the surface of the test specimen were heated by a Ripack 2000 gas heated gun until the white wax powder was melting and become transparent.

Cured for 12 hours at 20 degrees C, 65% relative humidity

25 Then solvent based graffiti paint was sprayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% relative humidity.

Observations:

30

The graffiti was easily removed by a brush and lukewarm water as well as by high pressure cleaning (water, 90-100 bar).

5 Comparison example D PTFE (1) Shamrock FLUORO AQ 60 – 60% aqueous dispersion of polytetrafluorethylene powder

10 The wax dispersion diluted by 50% of water by airless spray gun was applied on to the steel plates and dried for 3 hours. Then the surface of the test specimen was heated by a Ripack 2000 gas heated gun.

Cured for 12 hours at 20 degrees C, 65% relative humidity

15 Then solvent based graffiti paint was sprayed on to the coated surface and cured for 24 hours at 20 degrees C, 65% relative humidity.

Observation:

20 The graffiti was only partly removed by a brush and lukewarm water as well as by high pressure cleaning (90-100 bar), but the dispersion could not bond to the substrate and was easily removed by the said cleaning methods.

Conclusion:

25 The product is not useable for the intended purpose, presumably because the applied wax particles have not coalesced to a protective coating.

Example 4 (DISPERSION TEST)

30 To investigate the behaviour of PE-wax powders such powders were suspended in the carrier (Ethanol), and a series of test specimens (see below) were observed in an electronic microscope.

Test Specimens – Glass plates:

1. Davosi wax, PE (1) – mixed with Ethanol and sprayed on to a glass plate.
2. Davosi wax, PE (1) – mixed with Ethanol and sprayed and heated on to a glass plate.
3. Shamrock type S-394 SP5 wax – mixed with Ethanol and sprayed on to a glass plate
4. Shamrock type S-394 SP5 wax – mixed with Ethanol and sprayed and heated on to a glass plate.
5. Shamrock type S-394 N1 wax - mixed with Ethanol and sprayed on to a glass plate
6. Shamrock type S-394 N1 wax - mixed with Ethanol and sprayed and heated on to a glass plate

Observations:

From the observations it was evident that the wax powder was not dissolved in the ethanol. It was clear that the wax particles were intact in all the specimens where the various wax powders were mixed with ethanol.

Likewise it seems to be evident that after the heat treatment the wax particles were converted into a transparent, homogeneous, permanent very stable heat and chemical resistant sheet.

ADDITIONAL TESTS FOR ANTI-FOULING APPLICATIONS**Example 5 (Test with GRP-plate)**

A gel-coated GRP plate approx. 100 x 400 mm was treated on 50% of one side.

The wax mix (10 g of Davosi polyethylene wax powder in 1000 g of ethanol 96%) was applied by airless spray gun on to the steel plates and dried for 3 hours. Then the surface of the test specimen were heated by a Ripack 2000 gas heated gun until the white wax powder was melting and become transparent.

5

Cured for 12 hours at 20 degrees C at 65% relative humidity.

The test specimen was submerged into seawater in the Leisure Boat Marine in Bogense, Denmark for 30 days.

10

Observations after 30 days:

The non treated/coated surface was green from algae, sticking strongly to the surface.

15

The treated/coated surface seemed to be like slightly dusty after curing in open air, but the very fine particles (not algae) were easily removed by a soft hand.

Example 6 (Test with steel plate)

20

Test specimen: A black steel plate, dimensions: 150 x 150 mm.

50% of the one side (approx. 75 x 150mm) was coated.

25

The wax mix (10 g of Davosi polyethylene wax powder in 1000 g of ethanol 96%) was applied by airless spray gun on to the steel plates and dried for 3 hours. Then the surface of the test specimen were heated by a Ripack 2000 gas heated gun until the white wax powder was melting and become transparent.

30

Cured for 12 hours at 20 degrees C, 65% relative humidity

The test specimen was submerged into seawater in the Leisure Boat Marine in Bogense, Denmark for 30 days.

Observations after 30 days:

5

The non-treated/coated surface was heavily rusty and barnacled.

The treated surface was slightly dirty (easily removed by a brush and clean water), but the plate otherwise was not attacked by rust or algae.

10

TESTS FOR DIFFUSION OPENESS

Example 7

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Test 1.

A smooth concrete specimen with dimensions 100 x 200 x 10 mm was coated with a coating composition on all faces except for a circular area with a diameter of 40 mm. The coating composition was prepared by mixing 100 g of polyethylene wax powder type Davosi into 1 liter of ethanol 96%.

20

The coating composition was applied by airless spray gun and dried for 2 hours. It was observed that after evaporation of the carrier (ethanol) a white wax powder covered the surface of the sheet. Then a Ripack 2000 gas heated gun heated the surface until the white wax powder was melting and become transparent, and thereafter the coating was cured for 48 hours.

25

At the untreated circular area a glass tube with a diameter of 40 mm and a height of 600 mm was fixed in silicone mastic and cured for 24 hours.

The glass tube was filled with cold tap water and the concrete specimen was placed on four steel bolts with a diameter of 10 mm to lift the specimen from the table.

5 **Observations:**

After 4-5 seconds the first drops of water hit the table plate and the water was dripping through the concrete specimen with 1-2 drops per second.

Test 2:

10 A similar test as described in the above test 1 was carried out to see if more separate coatings could reduce or eliminate the diffusion openness.

15 A smooth concrete specimen with dimensions 100 x 200 x 10 mm was coated with a coating composition on all faces except for a circular area with a diameter of 40 mm. The coating composition was prepared by mixing 100 g of polyethylene wax powder type Davosi into 1 liter of ethanol 96%.

20 The coating composition was applied in three successive coating treatments by airless spray gun onto the surface. For each coating treatment it was observed that after evaporation of the carrier (ethanol) a white wax powder covered the surface. After the evaporation of the carrier the surface was dried for 2 hours. Then a Ripack 2000 gas heated gun heated the surface until the white wax powder was melting and become transparent, and cured for 48 hours. Each of the three coatings was applied with an interval of 6 hours.

25 At the untreated circular area a glass tube with a diameter of 40 mm and a height of 600 mm was fixed in silicone mastic and cured for 24 hours.

30 The glass tube was filled with cold tap water and the concrete specimen was placed on four steel bolts with a diameter of 10 mm to lift the specimen from the table.

Observations:

After 4-5 seconds the first drops of water hit the table plate and the water was dripping through the concrete specimen with 1-2 drops per second.

- 5 Conclusion: The diffusion openness is not reduced or eliminated if up to three coatings is applied.

TEST FOR CHEMICAL RESISTANCE10 **Example 8**

To test the chemical resistance the following test was carried out.
Specimens of concrete and marble with dimensions 97 x 35 x 10 mm were used in the test.

15

Solutions of hydrochloric acid were used on the specimens.

Specimen		Exposure	Observations
1	Coated concrete	30 minutes	No visual damages/deterioration
2	Coated concrete	20 hours	No visual damages/deterioration
3	Uncoated concrete	3 minutes	Heavy deterioration – 25%
4	Uncoated concrete	5 minutes	Very heavy deterioration 50%
5	Uncoated concrete	60 minutes	Only small stones left
6	Coated marble, one side only	6 minutes	Heavy deterioration on uncoated sides – 15% No Visual damages/deterioration on coated side
7	Coated marble, one side only	60 minutes	The marble completely disappeared. A very thin transparent sheet was observed floating in the acid solution.

TEST OF DURABILITY OF COATING ON A STEEL PLATE

20

Example 9

A coating composition was prepared by mixing 10 g of polyethylene wax powder Davosi into 1 liter of ethanol 96%. The coating composition was applied by airless spray gun onto half the area, denoted area 1, of a steel plate with dimensions 150 x 150 mm and dried for 3 hours. It was observed that when the ethanol had evaporated a white wax powder covered the surface. Then a Bosch air heated gun heated the surface until the white wax powder was melting and become transparent. The composition was cured for 12 hours at 20 °C, 65% relative humidity. A solvent-based graffiti paint was sprayed on to the total surface (area 1 + area 2) and cured for 24 hours at 20 °C, 65% relative humidity.

Observations:

The graffiti paint in area 1 was easily removed using a nail and/or a credit card. In area 2 a nail and/or a credit card could not remove the graffiti.

Continued test:

With two days interval the process of applying a new graffiti layer and removal of the cured graffiti paint was repeated. 50 repetitive layers of graffiti paint were applied/removed on the plate.

Observations:

The graffiti paint in area 1 was easily removed using a nail and/or a credit card. The graffiti paint in area 2 could not be removed using a nail and/or a credit card.

CLAIMS

1. A method of treating a surface comprising the steps of

5

- providing a coating composition comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase;

- applying said coating composition to the surface;

10

- evaporating said liquid phase from the applied coating composition; and

- subjecting said dried, applied coating composition to a heating treatment to coalesce said wax particles.

15

2. A method of providing a surface with a protecting coating by

- applying a coating composition in the form of a suspension comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase to the surface;

20

- evaporating said liquid phase from the applied coating composition;

25

- subjecting said dried, applied coating composition to a heating treatment to raise the temperature of the dried coating composition to bring said particles of a polyolefin wax or of a mixture of polyolefin waxes into a coalescing state allowing said wax particles to provide a continuous coating of the surface; and

30

- allowing said heat treated coating composition to consolidate to a protective coating.

5 3. The method according to any of the preceding claims wherein the liquid phase of the coating composition has a boiling point or a boiling point range lower than the melting point or melting point range of the particles of the polyolefin wax or of the mixture of polyolefin waxes.

10 4. The method according to any of the preceding claims wherein the liquid phase of the coating composition is organic.

15 5. The method according to any of the preceding claims wherein the liquid phase of the coating composition consists essentially of a member of the group consisting of ethers, esters, ketones, alcohols and mixtures thereof.

20 6. The method according to any of the preceding claims wherein the liquid phase of the coating composition comprises an alcohol, preferably ethyl alcohol.

25 7. The method according to claim 6 wherein the liquid phase of the coating composition comprises an alcohol, preferably ethyl alcohol and water

30 8. The method according to claim 7 wherein the concentration of water, calculated on weight basis, in the liquid phase is up to 50 %.

35 9. The method according to any of claims 1 to 3 wherein the liquid phase of the coating composition is essentially aqueous.

40 10. The method according to any of the preceding claims wherein the coating composition, calculated on weight basis, contains:

- polyolefin wax/mixture of polyolefin waxes 1 - 25 %, preferably 9 - 13 %,
- liquid phase 99 - 75 %, preferably 91 - 87 %.

- 5 11. The method according to any of the preceding claims wherein the coating composition comprises one or more auxiliary agents selected from the group consisting of diluting agents, dispersing agents, conservation agents, emulsifying agents, and colouring agents.
- 10 12. The method according to claim 11 wherein the coating composition, calculated on weight basis, contains up to 10% auxiliary agents.
- 15 13. The method according to any of claims 1 to 10 wherein the coating composition is consisting essentially of particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase.
- 20 14. The method according to any of claims 1 to 12 wherein the coating composition is consisting essentially of particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid organic or aqueous phase and one or more auxiliary agents selected from the group consisting of diluting agents, dispersing agents, conservation agents, emulsifying agents, and colouring agents.
- 25 15. The method according to any of the preceding claims wherein the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition are selected from the group consisting of polyethylene waxes, polypropylene waxes and oxidized and/or halogenated, in particular fluorinated polyethylene and polypropylene waxes.
- 30 16. The method according to any of claims 1 to 15 wherein the polyolefin wax is essentially a polyethylene wax.

17. The method according to claim 15 wherein at least one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polyethylene wax.

5 18. The method according to any of claims 15 to 17 wherein the polyethylene wax is having a degree of polymerisation between 10 and 500, in particular between 20 and 300, in particular between 30 and 200, in particular between 40 and 150, in particular between 40 and 100.

10 19. The method according to any of claims 15 to 18 wherein the particle size of the polyethylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

15 20. The method according to any of claims 15 to 19 wherein the peak melting point of the polyethylene wax is between 70 and 145°C, preferably between 80 and 140°C, in particular between 90 and 135°C, in particular between 95 and 120°C.

20 21. The method according to any of claims 15 to 20 wherein the polyethylene wax is consisting of essentially linear polyethylene.

22. The method according to any of claims 15 to 21 wherein the polyethylene wax is a high-density polyethylene, HDPE.

25 23. The method according to any of claims 15 to 22 wherein the polyethylene wax has a viscosity at 149 °C of 300 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less.

30 24. The method according to any of claims 15 to 23 wherein the polyethylene wax has a molecular weight distribution, M_w/M_n , of 1 to 25, preferably of 1 to 10,

preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2.

5 25. The method according to any of claims 15 to 24 wherein the polyethylene wax has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_w/M_n , of 6,0 or less, preferably has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_w/M_n , of 4,0 or less, more preferably has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_w/M_n , of 2,0 or less.

10 26. The method according to any of claims 1 to 15 wherein the polyolefin wax is essentially a polypropylene wax.

15 27. The method according to claim 15 wherein at least one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polypropylene wax.

20 28. The method according to claim 15 wherein one of the components in the mixture of polyolefin waxes suspended in the coating composition is a co-polymer of propylene and one or more other olefins not including propylene.

25 29. The method according to any of claims 15 or 26 to 28 wherein the particle size of the polypropylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

30 30. The method according to any of claims 15 or 26 to 29 wherein the peak melting point of the polypropylene wax is between 70 and 200°C, preferably between 100 and 170°C, in particular between 110 and 160°C, in particular between 120 and 150°C.

31. The method according to any of claims 15, 26 to 27, 29 to 30 wherein the polypropylene wax is consisting of essentially unbranched polypropylene molecules.

5 32. The method according to any of claims 15, 26 to 27, 29 to 31 wherein the polypropylene wax is characterised as consisting of essentially isotactic polypropylene molecules.

10 33. The method according to any of claims 15, 26 to 27, 29 to 31 wherein the polypropylene wax is characterised as consisting of essentially syndiotactic polypropylene molecules.

15 34. The method according to any of claims 15, 26 to 27, 29 to 31 wherein the polypropylene wax is characterised as consisting of essentially stereo block polymer structures, i.e. molecules having segments being syndiotactic or isotactic.

20 35. The method according to any of claims 15 or 26 to 34 wherein the polypropylene wax has a viscosity at 190 °C of 400 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less.

25 36. The method according to any of claims 15 or 26 to 35 wherein the polypropylene wax has a melt flow at 230 °C/2.16 kg of 40 g/min or more, preferably 100 g/min or more, preferably 500 g/min or more, preferably 1000 g/min or more, preferably 4000 g/min or more, preferably 8000 g/min or more.

30 37. The method according to any of claims 15 or 26 to 36 wherein the polypropylene wax has a molecular weight distribution, M_w/M_n , of 1 to 25, preferably of 1 to 10, preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2.

38. The method according to claim 15 wherein the polyolefin wax or one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polytetrafluorethylene wax.

5

39. The method according to claim 38 wherein the particle size of the polytetrafluorethylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

10

40. The method according to any of claims 38 to 39 wherein the melting point of the polytetrafluorethylene wax is between 250 and 360°C, preferably between 260 and 330°C, in particular between 280 and 320°C.

15

41. The method according to any of claims 1 to 14 wherein the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition consists essentially of one or more of the alkanes selected from the group of alkanes determined by the generic formula $\text{CH}_3\text{CHR}_1-(\text{CH}_2\text{CHR}_1)_n-\text{CHR}_1-\text{CH}_3$ for n equal to:

20

15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, where $\text{R}_1 = \text{H}$ or CH_3 .

25

42. The method according to any of claims 1 to 14 wherein the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition consists essentially of one or more of the alkanes selected from the group of alkanes determined by the generic formula $\text{CH}_3\text{CHR}_1-(\text{CH}_2\text{CHR}_1)_n-\text{CHR}_1-\text{CH}_3$ for n equal to:

30

49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140,

141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, where $R_1 = H$ or CH_3 .

43. The method according to any of claims 41 or 42 wherein the alkanes has a number of alkyl groups situated on the carbon backbone of the alkanes as branches, which number is 30 or less, preferably 20 or less, more preferably 10 or less, even more preferably 5 or less.

44. The method according to claim 43 wherein the alkyl groups situated on the carbon backbone of the alkane are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, preferably from the group consisting of ethyl, butyl, hexyl, octyl, more preferably from the group consisting of ethyl and butyl, yet more preferably is ethyl.

45. The method according to claim 41 or 42 wherein $R_1 = CH_3$ and all the methyl groups have the same stereochemistry.

46. The method according to claim 41 or 42 wherein $R_1 = CH_3$ and the stereochemistry changes from one methyl group to a neighbouring other methyl group.

47. The method according to claim 41 or 42 wherein $R_1 = CH_3$ and the molecular structure is a stereo block.

48. The method according to any of the preceding claims wherein the coating composition is applied to the surface by spraying.

49. The method according to any of the preceding claims wherein the coating composition is applied to the surface in an amount of 50 to 350 ml per m².

5 50. A coating composition comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase.

10 51. The coating composition according to claim 50 wherein the liquid phase of the coating composition has a boiling point or a boiling point range lower than the melting point or melting point range of the particles of the polyolefin wax or of the mixture of polyolefin waxes.

15 52. The coating composition according to any of claims 50 to 51 wherein the liquid phase of the coating composition is organic.

53. The coating composition according to any of claims 50 to 52 wherein the liquid phase of the coating composition consists essentially of a member of the group consisting of ethers, esters, ketones, alcohols and mixtures thereof.

20 54. The coating composition according to any of claims 50 to 53 wherein the liquid phase of the coating composition comprises an alcohol, preferably ethyl alcohol.

25 55. The coating composition according to claim 54 wherein the liquid phase of the coating composition comprises an alcohol, preferably ethyl alcohol, and water.

30 56. The coating composition according to claim 55 wherein the concentration of water, calculated on weight basis, in the liquid phase is up to 50 %.

57. The coating composition according to any of claims 50 to 52 wherein the liquid phase of the coating composition is essentially aqueous.

5 58. The coating composition according to any of claims 50 to 57 wherein the coating composition, calculated on weight basis, contains:

- polyolefin wax/mixture of polyolefin waxes 1 - 25 %, preferably 9 - 13 %,
- liquid phase 99 - 75 %, preferably 91 - 87 %.

10 59. The coating composition according to any of claims 50 to 58 wherein the coating composition comprises one or more auxiliary agents selected from the group consisting of diluting agents, dispersing agents, conservation agents, emulsifying agents, and colouring agents.

15 60. The coating composition according to claim 59 wherein the coating composition, calculated on weight basis, contains up to 10% auxiliary agents.

20 61. The coating composition according to any of claims 50 to 59 wherein the coating composition is consisting essentially of particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase.

25 62. The coating composition according to any of claims 50 to 60 wherein the coating composition is consisting essentially of particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid organic or aqueous phase and one or more auxiliary agents selected from the group consisting of diluting agents, dispersing agents, conservation agents, emulsifying agents, and colouring agents.

30 63. The coating composition according to any of claims 50 to 62 wherein the polyolefin wax or the components in the mixture of polyolefin waxes suspended

in the coating composition are selected from the group consisting of polyethylene waxes, polypropylene waxes and oxidized and/or halogenated, in particular fluorinated polyethylene and polypropylene waxes.

5 64. The coating composition according to any of claims 50 to 63 wherein the polyolefin wax is essentially polyethylene wax.

10 65. The coating composition according to claim 63 wherein one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polyethylene wax.

15 66. The coating composition according to any of claims 63 to 65 wherein the polyethylene wax is having a degree of polymerisation between 10 and 500, in particular between 20 and 300, in particular between 30 and 200, in particular between 40 and 150, in particular between 40 and 100.

20 67. The coating composition according to any of claims 63 to 66 wherein the particle size of the polyethylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

25 68. The coating composition according to any of claims 63 to 67 wherein the peak melting point of the polyethylene wax is between 70 and 145°C, preferably between 80 and 140°C, in particular between 90 and 135°C, in particular between 95 and 120°C.

30 69. The coating composition according to any of claims 63 to 68 wherein the polyethylene wax is consisting of essentially linear polyethylene.

30 70. The coating composition according to any of claims 63 to 69 wherein the polyethylene wax is characterised as high-density polyethylene, HDPE.

71. The coating composition according to any of claims 63 to 70 wherein the polyethylene wax has a viscosity at 149 °C of 300 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less.

72. The coating composition according to any of claims 63 to 71 wherein the polyethylene wax has a molecular weight distribution, M_w/M_n , of 1 to 25, preferably of 1 to 10, preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2.

73. The coating composition according to any of claims 63 to 72 wherein the polyethylene wax has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_w/M_n , of 6,0 or less, preferably has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_w/M_n , of 4,0 or less, more preferably has a molecular weight M_n in the interval of 400 to 3500 and a molecular weight distribution, M_w/M_n , of 2,0 or less.

74. The coating composition according to any of claims 50 to 63 wherein the polyolefin wax is essentially polypropylene wax.

75. The coating composition according to claim 63 wherein the polyolefin wax or one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polypropylene wax.

76. The coating composition according to claim 63 wherein one of the components in the mixture of polyolefin waxes suspended in the coating composition is a co-polymer of propylene and one or more other olefins not including propylene.

77. The coating composition according to any of claims 63 or 74 to 76 wherein the particle size of the polypropylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

5 78. The coating composition according to any of claims 63 or 74 to 77 wherein the peak melting point of the polypropylene wax is between 70 and 200°C, preferably between 100 and 170°C, in particular between 110 and 160°C, in particular between 120 and 150°C.

10 79. The coating composition according to any of claims 63, 74 to 75, 77 to 78 wherein the polypropylene wax is consisting of essentially unbranched polypropylene molecules.

15 80. The coating composition according to any of claims 63, 74 to 75, 77 to 79 wherein the polypropylene wax is characterised as consisting of essentially isotactic polypropylene molecules.

20 81. The coating composition according to any of claims 63, 74 to 75, 77 to 80 wherein the polypropylene wax is characterised as consisting of essentially syndiotactic polypropylene molecules.

25 82. The coating composition according to any of claims 63, 74 to 75, 77 to 81 wherein the polypropylene wax is characterised as consisting of essentially stereo block polymer structures, i.e. molecules having segments being syndiotactic or isotactic.

30 83. The coating composition according to any of claims 63 or 74 to 82 wherein the polypropylene wax has a viscosity at 190 °C of 400 mPa s or less, preferably 200 mPa s or less, preferably 150 mPa s or less, preferably 100 mPa s or less, preferably 70 mPa s or less, preferably 50 mPa s or less, preferably 40 mPa s or less.

84. The coating composition according to any of claims 63 or 74 to 83 wherein the polypropylene wax has a melt flow at 230 °C/2.16 kg of 40 g/min or more, preferably 100 g/min or more, preferably 500 g/min or more, preferably 1000 g/min or more, preferably 4000 g/min or more, preferably 8000 g/min or more.

85. The coating composition according to any of claims 63 or 74 to 84 wherein the polypropylene wax has a molecular weight distribution, M_w/M_n , of 1 to 25, preferably of 1 to 10, preferably of 1 to 5, preferably of 1 to 3, preferably of 1 to 2, preferably of 1 to 1.5, preferably of 1 to 1.2.

86. The coating composition according to claim 63 wherein the polyolefin wax or one of the components in the mixture of polyolefin waxes suspended in the coating composition is a polytetrafluorethylene wax.

87. The coating composition according to claim 86 wherein the particle size of the polytetrafluorethylene wax is between 0.1 and 100 μm , preferably between 2 and 25 μm , in particular between 4 and 20 μm .

88. The coating composition according to any of claims 86 to 87 wherein the melting point of the polytetrafluorethylene wax is between 250 and 360°C, preferably between 260 and 330°C, in particular between 280 and 320°C.

89. The coating composition according to any of claims 50 to 63 wherein the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition consists essentially of one or more of the alkanes selected from the group of alkanes determined by the generic formula $\text{CH}_3\text{CHR}_1-(\text{CH}_2\text{CHR}_1)_n-\text{CHR}_1-\text{CH}_3$ for n equal to:

15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, where $R_1 = \text{H}$ or CH_3 .

90. The coating composition according to any of claims 50 to 63 wherein the polyolefin wax or the components in the mixture of polyolefin waxes suspended in the coating composition consists essentially of one or more of the alkanes selected from the group of alkanes determined by the generic formula $\text{CH}_3\text{CHR}_1\text{-(CH}_2\text{CHR}_1)_n\text{-CHR}_1\text{-CH}_3$ for n equal to:

49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, where $\text{R}_1 = \text{H}$ or CH_3 .

91. The coating composition according to any of claims 89 or 90 wherein the alkanes has a number of alkyl groups situated on the carbon backbone of the alkanes as branches, which number is 30 or less, preferably 20 or less, more preferably 10 or less, even more preferably 5 or less.

92. The coating composition according to claim 91 wherein the alkyl groups situated on the carbon backbone of the alkane are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, preferably from the group consisting of ethyl, butyl, hexyl, octyl, more preferably from the group consisting of ethyl and butyl, yet more preferably is ethyl.

93. The coating composition according to claim 89 or 90 wherein $R_1 = \text{CH}_3$ and all the methyl groups have the same stereochemistry.

5 94. The coating composition according to claim 89 or 90 wherein $R_1 = \text{CH}_3$ and the stereochemistry changes from one methyl group to a neighbouring other methyl group.

95. The coating composition according to claim 89 or 90 wherein $R_1 = \text{CH}_3$ and the molecular structure is a stereo block.

10 96. Use of the coating composition according to any of claims 50 to 95 for treating a surface.

15 97. Use of the coating composition according to any of claims 50 to 95 for providing a surface with an essentially permanent anti-graffiti coating.

98. Use of the coating composition according to any of claims 50 to 95 for providing a surface with an essentially permanent coating protecting against pollution and corrosion.

20 99. Use of the coating composition according to any of claims 50 to 95 for providing an under water structure, e.g. a ship hull, with an essentially permanent anti-fouling coating.

25 100. An article of manufacture comprising a structure with a surface obtainable by the method according to any of claims 1 to 49.

101. An article of manufacture comprising a structure with a surface obtainable by use of the coating composition according to any of claims 50 to 95.

ABSTRACT

5 A method of treating a surface comprising the steps of providing a coating composition comprising particles of a polyolefin wax or of a mixture of polyolefin waxes suspended in a liquid phase; applying said coating composition to the surface; evaporating said liquid phase from the applied coating composition; and subjecting said dried, applied coating composition to a heating treatment to coalesce said wax particles.